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Significant improvement of the emission property of Spindt-type platinum field emitters by operation in carbon monoxide ambient

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The emission property of a Spindt-type platinum field emitter was greatly improved by operating in carbon monoxide ambient with appropriate operating parameters. After sufficient aging, the emitter was operated in carbon monoxide ambient up to 10^{-3} Pa, at the emission current of 1 μA. The emission current first decreased in accordance with the gas introduction, but turned to show rapid increase when the gas pressure was increased to 10^{-3} Pa. The current stability, as well as the operating voltage, was improved by this treatment. The apex of the emitter was examined with the Seppen–Katamuki analysis technique, in which detailed information on the emission area and effective work function can be read from the diagram plotted with the intercept and slope of a Fowler–Nordheim plot. The analysis suggested reduction of the effective work function is a major reason for the improvement of the emission property. © *2000 American Institute of Physics.* [S0003-6951(00)02430-X]

Nowadays, developments of flat-panel displays have been enthusiastically performed with plasma display panels and organic electroluminescence devices, as well as field emission displays (FEDs).[1] Among these displays, FED is one of the promising candidates that has high brightness, wider view angle, and high endurance against the operation circumstances, owing to the fact that the electron is taken out to the vacuum and accelerated easily. Although there are some new cathodes, the Spindt-type cathode[2] still locates at a closer position to the commercially available flat-panel display. One of the difficulties in realizing the FED is such that the field-emission device is generally unstable in poor vacuum conditions. Thus, development of a Spindt-type cathode with low-voltage operative and low-current fluctuation is a most important subject for the development of FEDs. Since the current fluctuation is mainly due to adsorption and desorption of the residual gas molecules,[3] the stability of the cathode is primarily dependent on the reactivity of the emitter surface. Studies have been made to obtain a cathode material which exhibits a superior property for Spindt-type cathodes.[4] We have also fabricated Spindt-type field emitters with different cathode materials and showed that platinum (Pt) exhibits a superior property among the element metals,[5] such as low-current fluctuation and low operating voltage. However, from circuitry requirements, further reduction of operating voltage is necessary. Although improvement with the deposition of metal or compound material onto Spindt-type cathodes was performed,[6,7] it is time consuming. Itoh, Niiyama, and Yokoyama have shown that the emission property of the Spindt-type molybdenum cathode was improved by operation in carbon monoxide (CO) gas.[8] The improvement reported was approximately a 10% increase of the emission current. Also, improvement was seen for a molybdenum emitter in hydrogen ambient.[9] We attempted to improve the Spindt-type Pt field emitters and found a significant improvement.

Platinum one-tip emitters were fabricated by our process,[10] which is based on the process developed by Spindt *et al.*[2] The sample was mounted on TO-5. The gate electrode was grounded and the negative bias was applied to the emitter. The emission current was monitored by an external collector settled at 5 mm above the sample. The collector was biased to positive 200 V. All the measurements were performed in dc mode. The entire system was installed in the vacuum vessel, which was pumped by a sputter ion pump and a titanium sublimation pump. The base pressure of the vacuum vessel is 10^{-7} Pa.

Prior to detailed measurement, the emitter was first aged in ultrahigh vacuum (UHV) for about 6–12 h to stabilize the emission current. We repeated the current–voltage characteristics measurement and the current fluctuation measurement alternatively. In this sequence, we increased the maximum current in the current–voltage characteristics gradually. A maximum current of approximately 20 μA was sufficient to stabilize the emission current.

After the aging was performed, the emitter was operated in UHV for about 150 h. Although the characteristics slightly deviated, an emitter voltage of 58 V was necessary to extract 40 nA current.

After the above operation, the emission current was adjusted to be 1 μA, and carbon monoxide (CO) gas was introduced to the measurement vessel. First, CO gas was introduced to 10^{-5} Pa. At this stage, only a slight decrease of the emission current was observed during the 30 min operation. After the above exposure, CO gas was once evacuated and the current–voltage characteristics were measured. Second, CO was introduced to 10^{-4} Pa, and the emission current fell

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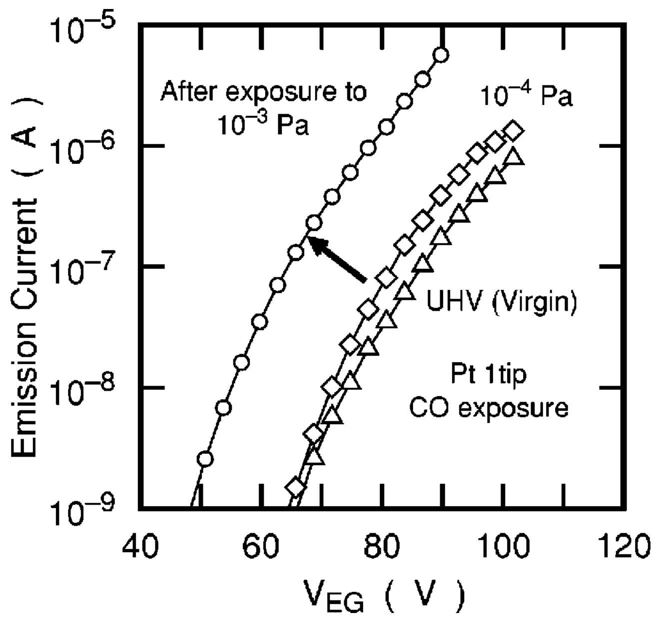

FIG. 1. Current–voltage characteristics of one-tip Spindt-type Pt field emitter before and after exposure to CO gas.

down to 0.1 μA, also during the 30 min operation. Finally, CO gas was introduced to 10^{-3} Pa, and the emission current tended to increase rapidly, exceeding the initial current of 1 μA. The operation was then interrupted and the CO gas was evacuated.

Figure 1 shows the current–voltage characteristics of the Pt emitter before exposure to CO, after exposure to 10^{-4} Pa

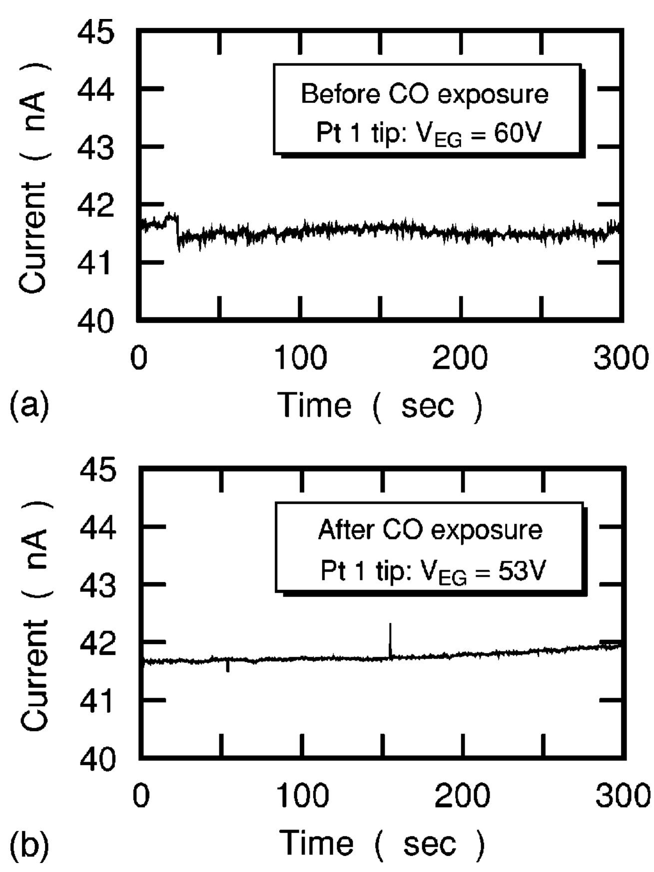

FIG. 2. Current fluctuation of the Pt emitter (a) before and (b) after exposure to CO gas.

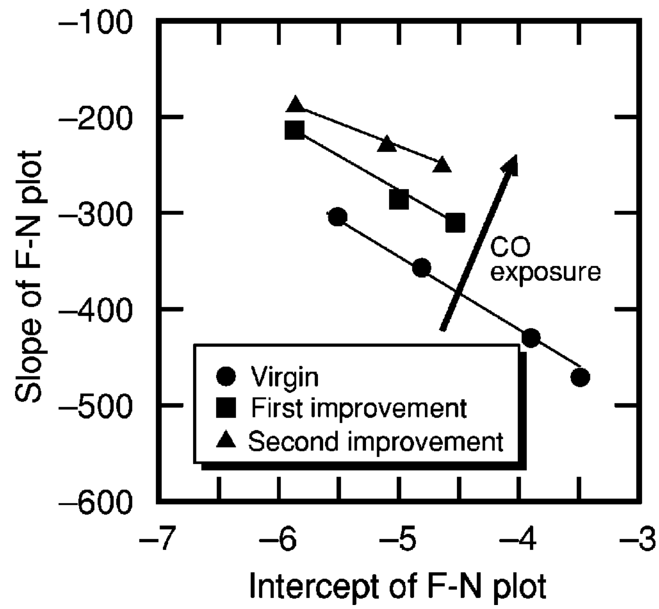

FIG. 3. Analysis of the surface state of Pt emitters with the Seppen–Katamuki chart.

CO, and after exposure to 10^{-3} Pa CO. All measurements of the current–voltage characteristics mentioned in the present study were done after evacuation of the CO gas. It is clearly seen that the emission current significantly improved by a factor of 2 orders of magnitude. The operating voltage for 40 nA extraction was reduced to 40 V, which is approximately a 30% reduction. The effect of the improvement was larger than the case of the molybdenum emitter with methane.[8] The effect of this modification lasted more than 200 h. The improvement of the molybdenum cathode in hydrogen ambient did not continue for such a long time.[9] Reduction of the operating voltage significantly reduces the difficulty in the design of the driving circuit.

As well as reduction in the operating voltage, the current fluctuation was lowered by this treatment. Figures 2(a) and 2(b) show the current fluctuation before and after the CO exposure. Before exposure, the current fluctuation was seen but after exposure, the fluctuation was lowered. We estimated the current fluctuation with the normalized noise power, which can be calculated by integrating the power spectral density of the current fluctuation between 0.2 and 2 Hz.[11] The noise power before exposure was 1.4×10^{-5} (–49 dB) and after exposure was 1.6×10^{-6} (–58 dB). These improvements were seen for the initial current of 1 μA, but not for that of the other currents.

The reason for reduction of the operating voltage was analyzed with a Seppen–Katamuki (SK) chart, in which the intercept (Seppen) and the slope (Katamuki) of the emission characteristics in a Fowler–Nordheim (FN) plot are taken for the abscissa and ordinate. Generally, the evaluation of a field emitter is performed with the slope of the FN plot using a well-defined emitter as the standard. However, it is difficult to evaluate a deposited field emitter because we do not have a standard that can be obtained, for example, by flashing. We have found an empirical relation[12,13] between the slope and the intercept of the FN plot for emitters of the same materials: The characteristics distribute along a line downward to the right. We can estimate the relative change of the surface state from the location in this diagram. The present understanding is such that motion to the upper right and that to the lower left shows a decrease and increase of the effective work function, and motion to the upper left and that to the lower right shows a decrease and increase of the apex radius.[12,13] Figure 3 shows the SK chart before and after improvement. Before improvement, the characteristics of the emitter in UHV operation located along the line shown by the closed circles, which agrees with the tendency seen for the other deposited emitters.[12] After exposure, the characteristics were changed to those shown by the closed squares. Since the characteristics moved toward the upper right, it was suggested that the effective work function was reduced by the operation in the CO gas ambient. The second improvement also showed a further decrease of the work function, as shown in Fig. 3 by the closed triangles.

In most emitters, including metal,[11] diamond,[14] and transition-metal nitrides,[15,16] the current fluctuation is closely related to the work function or the operating voltage. The present result agreed with these results. The reason why we could decrease the work function remains unknown. That the decomposition of the CO gas due to electron impact resulted in the deposition of carbon atoms on the Pt emitter is one plausible reason for reduction of the work function.

In summary, we have improved the emission properties of a Spindt-type Pt field emitter by exposing the emitter to CO gas ambient during operation. We conclude the improvement of the emission property is entirely attributed to the reduction in the effective work function of the Pt emitter.

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